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Dynamics of optical phonons in Bi_2Se_3 crystal studied using femtosecond time-resolved reflection measurement

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Abstract. The dynamics of coherent optical phonons (A_{1g}^1, A_{1g}^2 and E_g^2) in Bi_2Se_3 single crystal have been observed by using femtosecond time-resolved reflection measurement. The phonons with the higher frequency have the faster damping rate (decay faster). The A_{1g}^2 phonons show cosine-like oscillation, while the A_{1g}^1 and E_g^2 phonons show cosine-like oscillation. The difference in the initial phase suggests that the potential energy surface may shift significantly along the A_{1g}^2 eigenvector and little along the A_{1g}^1 and E_g^2 eigenvectors in the excited state.

1 Introduction

Recently, Bi_2Se_3 has attracted considerable attention in materials science because it is not only the well known bulk thermoelectric materials but also recognized as a topological insulator [1]. Among bismuth chalcogenides, Bi_2Se_3 stands out due to its simple Dirac-like surface states and relatively greater band gap of ~0.3 eV. Even though its phonon properties have been studied extensively by using Raman spectroscopies [2,3], the dynamical investigations are lacking and desired. Dynamics of phonons including phonon-phonon and phonon-carrier couplings can be studied by time-domain spectroscopy. In this work, we studied the dynamics of optical phonons in a Bi_2Se_3 single crystal using the femtosecond time-resolved reflection measurement. Coherent optical phonon modes (A_{1g}^1, A_{1g}^2, and E_g^2) have been observed at room temperature. Their decay rates per oscillations are almost the same. The coherent A_{1g}^1 and E_g^2 phonons and A_{1g}^2 are sine-like and cosine-like, respectively. The initial phases suggest that the potential energy surfaces shift in direction of A_{1g}^2 eigenvector by photoexcitation.

2 Experimental details

The femtosecond time-resolved reflectivity measurement was performed using a conventional pump and prove technique at room temperature and in the air. The light source was a mode-locked Ti:sapphire laser with a wavelength centered at 800 nm (~1.55 eV), providing ~40 fs pulses at a repetition rate of 86 MHz. The output of the laser was supplying an average power of 20 mW for the pump beam and 2 mW for the probe beam. The spot size of them was kept ~30 μm at the overlap of

the two beams on the sample. The polarization of the pump and probe beams was orthogonal to prevent scattered pump light from reaching the detector. The change of temporal evolution of the reflectivity change was measured by scanning the probe delay t repetitively at 20 Hz with a fast-scan mechanical stage. Isotropic reflectivity ($\Delta R/R$) and anisotropic reflectivity ($\Delta R_{eo}/R=(\Delta R_p-\Delta R_s)/R$) measurements were performed. In the anisotropic reflectivity measurements, we used the electro-optic (EO) sampling method, in which the incident probe beam was polarized 45 degrees with respect to the optical plane. After reflection from the sample, the probe beam was analyzed into p- and s-polarized components and detected with the matched photodiodes to remove the isotropic components of the reflectivity change. The sample was a single crystal of Bi_2Se_3 grown by a modified Bridgman technique [1]. The bandgap of Bi_2Se_3 is approximately 0.3 eV. A fresh surface parallel to the rhombohedral (001) plane was obtained by cleaving the sample with an adhesive tape.

3 Results and discussion

The anisotropic reflectivity change consists of two components: one is an oscillatory part caused by the coherent phonons, and the other is a non-oscillatory background component arising from electrons photo-excited to higher energy bands (initial response) and lattice heating due to electron-lattice coupling. The oscillatory behaviors as a function of the time delay between the probe and pump pulses. By subtracting the non-oscillatory background modulation, a beat structure is found in the oscillation (Fig. 1). The oscillatory part of the transient reflectivity change ($\Delta R_{eo}(t)/R$) was analyzed with three damped oscillations:

$$\Delta R_{eo}(t)/R = \sum_{i=1,2,3} A_i exp(-t/\alpha_i) sin\,(\omega_i t - \theta_i) \quad (1)$$

where A_i is an amplitude, α_i is the lifetime, ω_i is the frequency, and θ_i is the initial phase. The result of the fitting is also shown in Fig.1, and the parameters are listed in Table 1.

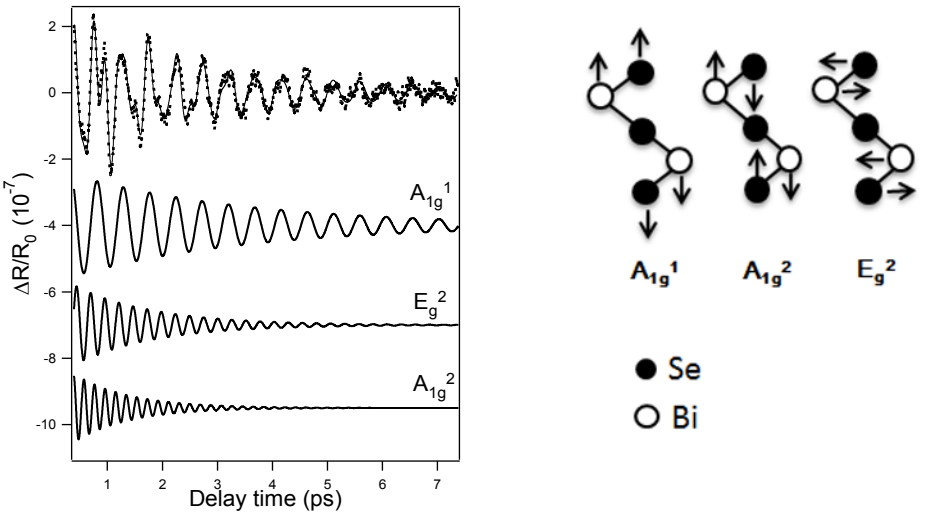

Fig. 1. The oscillatory part of the time-resolved reflectivity change: the experimental data (dot-line) and the result of curve fitting with three damped oscillations (solid line) expressed by Eq. (1). Three vibrational modes are also shown in the right.

Bi_2Se_3 has the rhombohedral crystal structure and five atoms in a primitive unit cell, and then there are twelve vibrational modes. Chen and Ren [4] have calculated phonon dispersion curves of the

Bi_2Se_3 film and bulk material using *ab initio* calculations with spin-orbit coupling and reported four Raman active modes E_g^1, A_{1g}^1, E_g^2 and A_{1g}^2 at frequencies of 1.166, 1.914, 3.717 and 4.987 THz at the Γ point. The calculated frequencies agree well with those observed by Raman spectroscopy [2]. The observed oscillations in our experiment at frequencies of 2.09, 3.90, and 5.20 THz were assigned to the coherent phonons with A_{1g}^1, E_g^2, and A_{1g}^2 phonons, respectively. The A_{1g} phonons are totally symmetric mode and the E_g mode is asymmetric.

Table 1. Parameters obtained by curve fitting with three damped oscillations

Mode	Initial amplitude (1E-7)	Frequency (THz)	Lifetime (ps)	Initial phase (rad)
A_{1g}^1	1.72	2.09	3.22	0.90
E_g^2	1.58	3.90	1.43	0.93
A_{1g}^2	1.53	5.20	0.99	0.53

The result of the fitting is also shown in Fig.1, and the parameters are listed in Table I. The higher frequency phonons have shorter lifetimes. However, the reduction of phonons per oscillation is almost the same: 0.86, 0.82, and 0.84 for A_{1g}^1, A_{1g}^2, and E_g^2 modes, respectively. Therefore, the relaxation process might be the same for these optical phonon modes. The most pronounced difference in phonon dynamics is the initial phase. The A_{1g}^1 and E_g^2 phonons are sine-like oscillations, while the A_{1g}^2 phonon is a cosine-like oscillation. A similar phase difference between the A_{1g} and E_g phonons has also been observed in previous studies on Bi and Sb [5]. The differences of initial phase are probably due to potential energy surfaces for exited state. The cosine-like oscillation is distorted by strong couplings between phonons and photo-excited electrons. On the other hand, the electron-phonon couplings are negligible in the sine-like oscillations.

4 Summary

Coherent A_{1g}^1, A_{1g}^2, and E_g^2 phonons in Bi_2Se_3 are observed using ultrafast transient transmission measurements. Their decay rates per oscillations are almost the same. The coherent phonons with A_{1g}^2 mode and A_{1g}^1 and E_g^2 modes are cosine-like and sine-like, respectively. The initial phases suggest the potential surfaces in photo-excited states shift in the direction of A_{1g}^2 eigenvector by photoexcitation.

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